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Alberta Hydrogen Research Program

Annual Review 1992/93

Alberta
ENERGY
Research and Technology Branch

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Director's Report

Hydrogen is an important commodity in Alberta; its production alone contributes $500 million to $600 million to the economy each year.

Furthermore, hydrogen is used in the ammonia, methanol, petroleum and chemical industries, which collectively contribute several billion dollars annually to Alberta's economy. Since the products from these industries are sold in world markets, their prices are under constant pressure from competitors. This means that manufacturers are always seeking to lower production costs and raise production efficiencies. One way these two goals can be achieved is to make one of the required feedstocks—hydrogen—available at lower prices, and to improve the way that hydrogen is used in these various processes.

Nearly 230,000 tonnes of hydrogen, 17 per cent of the annual production, are wasted each year. They either vented, flared or used as fuel. This hydrogen could be used if a collection systems and pipeline system existed to transport it to users from the point of production. Thirteen per cent of this surplus hydrogen is more than 90 per cent pure; the rest is between 50 per cent and 90 per cent.

Superimposed on this situation are other realities. For example, the steam-methane reforming method used to make hydrogen is the cheapest known commercial process in Alberta. However, it consumes a non-renewable resource (natural gas), and carbon dioxide is generated as a by-product of the process.

Upgrading processes that are evolving for bitumen treatment and to meet new refinery standards will require more hydrogen than is now used. This means that hydrogen-production costs must come down.

Taking all these issues into consideration, the principal focus of the Alberta Hydrogen Research Program is to help make Alberta's energy industry more efficient and to use hydrogen as a principal link for integrating the oil and gas industry and diversifying the province's industrial base.

It is appreciated that this approach differs from that used in hydrogen research activities in many other parts of the world where the emphasis is on hydrogen as a fuel and energy commodity. In Alberta's case, however, it is believed that all the components needed to produce, distribute and use hydrogen safely, more efficiently and at less cost by industry are the same elements needed to position Alberta at the forefront of the hydrogen-fuel industry.

While the program supports research activities in aspects of hydrogen production, storage, transportation, purification and consumption, much of the early emphasis has been on developing a commercial process for producing hydrogen from hydrogen sulphide (H_2S) gas. Hydrogen sulphide gas is widely available in Alberta, either present in many natural gas deposits or generated as a by-product of heavy oil and bitumen upgrading or petroleum refining.

A commercial process for dissociating H_2S into its two components—hydrogen and sulphur—will produce two valuable commodities from an otherwise hazardous chemical and will not produce other harmful environmental emissions as by-products.

The removal of sulphur (called hydro-desulphurization) from heavy oil and bitumen generates significant quantities of H_2S. In addition, sour gas treatment plants around Alberta remove H_2S from natural gas. All these facilities convert H_2S to sulphur and water using the Modified

Claus Process. Based on the 580 000 tonnes of sulphur produced each year from Alberta's oil sands, recovering and recycling hydrogen from the H_2S produced during hydrodesulphurization alone could generate annual savings of up to $18 million.

In addition, the normal bitumen upgrading process uses approximately 1 200 standard cubic feet (scf) of hydrogen for each barrel of bitumen. Hydrogen is the single most important cost in the upgrading of bitumen. Future high-conversion processes are expected to use approximately 2 200 scf of hydrogen per barrel of bitumen. Given the current low prices for oil, less-expensive hydrogen and more-efficient use of it are needed to help make synthetic crude oil competitive.

The Alberta Hydrogen Research Program has now completed its fourth year of operation, with a total of 28 research projects initiated. Thus far, the projects have related directly to the production or use of hydrogen in current Alberta industries. All were proposed and partly supported by these industries. More than a year ago, industry contributions to project funding reached the 50 per cent level, where they remained this year.

Among the developments this year was a new project aimed at making hydrogen peroxide (H_2O_2) by directly oxidizing hydrogen. This commodity is being used increasingly in Alberta's expanding pulp and paper industry to alleviate concerns about dioxins in pulp mill effluents. The commercial production of H_2O_2 from hydrogen could represent a major new secondary industry for the province.

The annual workshop, where project operators give presentations on the progress they have made during the past year, was once again well attended by industry representatives. This show of interest, combined with the ongoing financial support by industry for the program, is much appreciated.

M.E. Torres

Director, Alberta Hydrogen
Research Program

Introduction

During 1987/88, a study to quantify current hydrogen production and consumption in Alberta revealed that Alberta industries produce 55 per cent and consume 63 per cent of all the hydrogen in Canada.

It was noted that most of the anticipated growth in hydrogen use is expected to arise from upgrading heavy oil and bitumen. Because the costs of hydrogen production currently represent a significant portion of overall upgrading costs, and the energy industry had previously expressed interest in working with government to lower these costs, a joint industry/government hydrogen technology research and development program was initiated in 1988/89. It has been funded ever since by government and industry.

Currently, hydrogen production, transportation and use are the three priorities of the Alberta Hydrogen Research Program. Each of the following program components represents an aspect of hydrogen technology for which commercial-scale development within 10 years is desirable.

The components are:

- advanced or alternative hydrogen-production technologies;
- hydrogen separation technologies;
- large-volume hydrogen storage;
- transportation/distribution of hydrogen;
- optimum end-uses of hydrogen; and
- materials and safety technology.

Despite limited funds available from the government the number of research projects supported by the program has grown steadily. This growth was only possible with the industry assuming a greater share of research costs. In 1989/90, there were only seven projects. This grew to 13 in 1990/91, then to 20 in 1991/92, and 30 for this year. Including the hydrogen technology inventory study that started it all, and was completed in 1988, 31 projects have been funded thus far.

The following section, Review of Program Projects—1992/93, provides detailed information about individual projects and their achievements. The financial aspects of past and present projects are found in Appendix B.

Hydrogen Consumption in Alberta (tonnes/year)

Process	Consumption	%
Chemical		
Ammonia	512 700	38.5
Methanol	225 400	16.9
Oil Sands	260 400	19.5
Refining	91 700	6.9
Other Chemicals	7 600	0.6
Miscellaneous	1 400	0.1
Fuel		
Ammonia	2 200	0.2
Methanol	129 600	9.7
Oil Sands	13 200	0.9
Refining	21 100	1.6
Other Chemicals	46 600	3.5
Miscellaneous	200	—
Venting, Incineration	20 700	1.6
Total	1 332 800	100.0

Review of Program Projects—1992/93

Hydrogen Production

Water (H_2O), methane (CH_4) and hydrogen sulphide (H_2S) are considered to be the three most likely sources for hydrogen production in the immediate future in Alberta. This does not imply that all other potential sources are excluded. It means that these three feedstocks represent the richest, cheapest and most readily available sources.

Although, steam-methane reforming (SMR) is the most important and best developed hydrogen production method in Western Canada, it is not necessarily the only option for Alberta. It also generates carbon dioxide as a by-product, a fact that is of some concern to a world worried about atmospheric warming.

Nonetheless, whenever alternative hydrogen production technologies are proposed, they are compared to SMR. This comparison requires evaluation of several factors, including process chemistry, energy input, process engineering, product separation and purification, and by-product uses.

In the following section on hydrogen production research, six projects are described. All represent attempts to develop new or improved hydrogen-producing systems that have commercial potential in the near future.

Thus far, all these investigations have focused on making hydrogen from hydrogen sulphide for the following reasons: the gas is abundant in Alberta; it must undergo some form of treatment before it is released to the environment; the current treatment method recovers only one of the two possible commodities; and hydrogen production from hydrogen sulphide does not release carbon dioxide. This last characteristic, which is common to processes that electrolyse water to make hydrogen and oxygen, is often touted as the principal advantage of electrolysis over SMR.

CONVENTIONAL SOURCES OF HYDROGEN

$$H_2O \xrightarrow{\text{Electrolysis}} H_2 + \tfrac{1}{2}O_2$$

$$CH_4 + 2H_2O \xrightarrow{\text{Steam-Methane Reforming}} CO + 3H_2 + H_2O \xrightarrow{\text{Shift Conversion}} CO_2 + 4H_2$$

$$C + 2H_2O \xrightarrow{\text{Coal Gasification}} CO + H_2 + H_2O \xrightarrow{\text{Shift Conversion}} CO_2 + 2H_2$$

A Claus Plant Modification for Hydrogen Production[1]

ALBERTA SULPHUR RESEARCH LTD., CALGARY

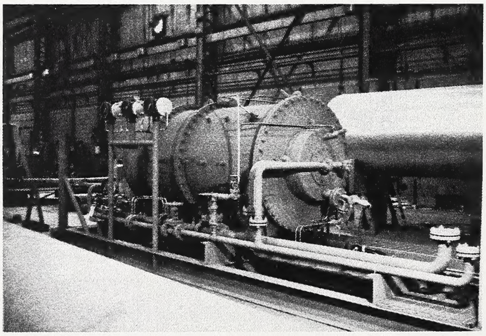
After four years' work, a process for producing hydrogen from hydrogen sulphide (H_2S) is about to move from the laboratory to field trials.

The concept involves using excess heat from existing Modified Claus plants to crack H_2S and produce sulphur (S) and hydrogen (H_2) instead of the sulphur (S) and water that are produced now. These plants, which are found throughout Alberta at sour gas operations, refineries and heavy oil/bitumen upgraders, generate the temperatures necessary to crack H_2S to hydrogen and sulphur. This has been demonstrated in hundreds of laboratory studies at Alberta Sulphur Research Ltd. (ASRL). The challenge is to obtain the highest possible conversion of H_2S to sulphur and hydrogen, and prevent back reactions from occurring that will cause these products to recombine.

Although experiments have shown that the cracking reaction can occur at temperatures as low as 800°C, and the presence of a catalyst will reduce the reaction time from seconds to milliseconds, the most desirable option is to use a reaction temperature above 1 100°C. Under this condition, hydrogen yields of 25 per cent have been measured in the laboratory. This corresponds well with temperatures normally found in the flame box zone of a typical Claus plant (1 100°-1 300°C). This will be the temperature range sought in a pilot-scale mini-Claus cracker that will be field-tested during the summer of 1993.

The laboratory studies also showed that rapidly lowering the temperature to 600°C after H_2 and S had formed effectively quenched the back reaction. The quicker this was done, the higher the yield of H_2. For example, the theoretical yield for an acid gas mixture comprising 90 per cent H_2S and 10 per cent CO_2 is 32 per cent at 1 200°C. A quench time of 0.05 seconds produced an actual yield of 24 per cent. When the quench time was extended to 0.15 seconds, however, the yield decreased to 15 per cent. The ideal situation is to separate the H_2 and S at the cracking temperature. The approach being taken is to develop porous ceramic membranes that will preferentially allow hydrogen to pass through, thus effectively removing it from further reaction. Initial results using "doped" commercial membranes are promising.

Laboratory studies at ASRL have considered the effects of impurities in the feed gas. Tolerable limits have been established for the substances that are most likely to be present in the feed to a Claus plant. While it was shown earlier that CO_2 in concentrations up to 10 per cent has no effect on the H_2 yield, methane interferes with the cracking process at concentrations greater than one per cent. This effect, however, can be reduced if CO_2 is present. No potential interference was observed when ammonia was introduced in concentrations normally found in refinery feed.



Skid-mounted mini-Claus plant to be used for H_2S dissociation experiments. (Photo courtesy of Alberta Sulphur Research Ltd.)

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[1] The project received financial support from Alberta Sulphur Research Ltd. and the Alberta Department of Energy. In previous years, support was provided by the Alberta/Canada Energy Resources Research Fund, administered by the Alberta Department of Energy.

Computer studies have indicated how much of the incoming feed gas can be split between a retrofitted cracker and the Claus plant. A balance is necessary since the Claus plant operating temperature depends on having sufficient quantities of H_2S feed.

At year-end, a skid-mounted mini-Claus furnace was being built by Maloney Steel Ltd. of Calgary. It comprises four flanged sections for the burner, combustion chamber, cracker and tube sheet. The furnace is fitted with numerous thermocouple ports, sampling ports and sight tubes.

The first field trial of the minifurnace will be at the Wildcat Hills operation of Petro-Canada Resources.

Publications

Dowling, N.I. and J.B. Hyne. 1993. A Claus Furnace Modification to Produce Both Sulfur and Hydrogen from H_2S. Sulphur '93, Hamburg, Germany. April 4-7.

Dowling, N.I., J.B. Hyne, D.L. Moon and C.S.C. Lau. 1993a. A Claus Plant Modification for Hydrogen Production. Report for October-December 1992. Alberta Sulphur Research Ltd.

Dowling, N.I., J.B. Hyne, D.L. Moon and C.S.C. Lau. 1993b. A Claus Plant Modification for Hydrogen Production. Report for January-March 1993. Alberta Sulphur Research Ltd.

Dowling, N.I., J.B. Hyne, D.L. Moon and C.S.C. Lau. 1992. A Claus Plant Modification for Hydrogen Production. Final A/CERRF Report.

The Carbon Monoxide Catalyzed Conversion of Hydrogen Sulphide to Hydrogen and Sulphur[1]

UNIVERSITY OF ALBERTA, EDMONTON

In processes that use thermal dissociation to produce hydrogen and sulphur from hydrogen sulphide (H_2S), high temperatures are needed to drive the equilibrium reaction ($H_2S \leftrightharpoons H_2$ + sulphur) sufficiently to the right so that significant quantities of the reaction products will be produced. The objective of a research project under way at the University of Alberta is to establish lower-temperature and economic reaction conditions to accomplish the same thing. One conceivable way to achieve this goal is the following two-step consecutive reaction sequence:

$$H_2S + CO \leftrightharpoons H_2 + COS \qquad \Delta H_{rxn} = -2.6 \text{ kcal/mol} \tag{1}$$

$$COS \leftrightharpoons CO + \text{sulphur} \qquad \Delta H_{rxn} = +10.5 \text{ kcal/mol} \tag{2}$$

Both steps have been studied at the University of Alberta since 1990. Because they are equilibrium reactions, it was found that they can be enhanced by using an appropriate catalyst.

Reaction (1) can be brought nearly to equilibrium between 200°C and 300°C in one minute, giving approximately 25 per cent conversion in a mixture of H_2S and carbon monoxide (CO) at 0.5 atmosphere, each. Higher H_2S conversion can be obtained when CO is used in excess.

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[1] Funding was provided this year by the National Science and Engineering Research Council, Canadian Occidental Petroleum Ltd. and the Department of Energy.

Reaction (2) requires a higher temperature. At 700°-750°C, under appropriate conditions, the reaction can give approximately 50 per cent conversion per pass with residence times of less than one minute.

During 1992/93, both reaction steps were optimized in preparation for an economic feasibility assessment. Full details of the reaction conditions cannot be published, as patent protection is being sought. Nonetheless, all steps in the proposed process rely on well-known, conventional technologies requiring simple equipment and low-cost, durable catalysts.

Under the best conditions thus far, reaction (1) produced a 67.2 per cent conversion of H_2S at 177°C.

The project will continue next year.

Publications

Strausz, O.P. 1993. The CO-Catalyzed Conversion of H_2S to H_2 and S. Final Report. April 1, 1992 - March 31, 1993. University of Alberta.

Torres, M.E., E. Yildirim, F. Faraji and O.P. Strausz. 1993. Novel Processes for the Conversion of H_2S to H_2 and S. Proceedings of Oil Sands: Our Petroleum Future Conference, April 4-7, 1993. Edmonton, Alberta.

Cold Plasma Decomposition of Hydrogen Sulphide[1]

SHELL CANADA LIMITED (CALGARY) AND ATOMIC ENERGY OF CANADA LIMITED RESEARCH COMPANY (CHALK RIVER)

Many different processes have been explored in the laboratory to dissociate hydrogen sulphide (H_2S). Because the energy of dissociation of H_2S is so much lower than that of water, H_2S promises to be a cheap source of hydrogen. Yet none of the various attempts to produce hydrogen in this manner has reached the commercial scale.

Using microwave energy to dissociate H_2S is a relatively new approach. Pioneering work by Russian scientists in the mid-'80s indicated good conversions and energy use. Shortly after that, experimental work began at the Chalk River laboratories of Atomic Energy of Canada Limited (AECL). The project was joined by Shell Canada Limited and received some funding from the Alberta Hydrogen Research Program.

Shell Canada Limited is a major user of hydrogen in its refineries and will need hydrogen at a potential heavy oil or oil sands upgrader. The hydrogen is needed to remove objectionable crude oil components, such as sulphur, nitrogen and unsaturates, and to produce high-quality fuels. Shell also produces large amounts of H_2S, mainly by natural gas processing in Alberta. If the hydrogen contained in the produced H_2S could be made available, it would be equivalent to most of Shell's hydrogen requirements in the province.

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[1] The project was funded by Shell Canada Limited, Atomic Energy of Canada Limited and the Alberta Department of Energy.

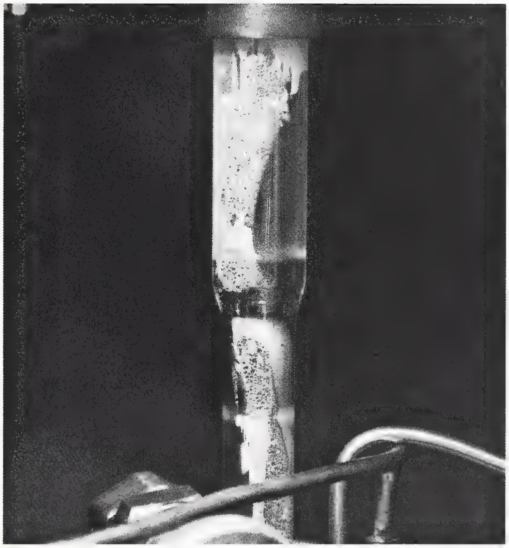
Exposure of H_2S to microwave radiation at low pressures creates a "cold plasma" in which the electrons have a higher temperature than the bulk phase. Dissociation of H_2S takes place, and even at pressures approaching atmospheric, an effluent is produced that has a relatively low temperature (less than 1 000°C). Thus, the opportunity for sulphur and hydrogen to recombine is significantly reduced. This represents a major advantage over thermal processes, in which rapid quenching or separation at high temperatures is needed to avoid recombination.

Significant progress has been made in the joint research program since it started in 1989. Pure H_2S conversion and energy use have been measured at different conditions. Commercial H_2S streams are never pure, however. Accordingly, the effects of carbon dioxide (CO_2) and methane (CH_4) on hydrogen production have been measured. Theoretically, the process works best at pressures well below atmospheric, but this means high pumping costs for a commercial process. The effects of pressure were studied in the laboratory, and they showed that operating at or near atmospheric pressure is possible. This will save pumping energy, but will cause some reduction in the reaction efficiency.

Concurrently with this work, scientists at the Kurchatov Institute in Russia have implemented plasmolysis of H_2S at a gas plant near Orenburg, Russia. The plant is a one megawatt unit and has a sulphur capacity of approximately 35-40 tonnes per day. A 5-MW unit is planned.

Argonne National Laboratories in the U.S. has pursued an experimental program in this area and recently had extensive discussions with the Russians. The focus now is on the economics of the process and the possibility of constructing a demonstration plant to verify the Russian experience, a concept that is being promoted by the Hydrogen Industry Council.

Given these major advances in H_2S plasmolysis technology, AECL and Shell are closely monitoring developments in anticipation that implementation in Alberta will make a contribution to the provincial hydrogen supply.



When a hydrogen sulphide plasma decomposed, one of the products--sulphur--deposited on the walls of the reactor. (Photo courtesy of AECL Research).

Publications

Craw, M.T., K.D. McCrimmon, R.P. Tremblay, R.M. Hutcheon and E. Luinstra. 1992. Microwave Decomposition of Hydrogen Sulphide. 10th Anniversary Conference, Hydrogen Industry Council. Kananaskis, Alberta, May 20-21. 1992.

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Craw-Ivanco, M.T. and E. Luinstra. 1992. Cold Plasma Decomposition of Hydrogen Sulphide. H_2 Workshop '92. Calgary, Alberta, October 8, 1992.

Craw-Ivanco, M.T. and J.H. Rowat. 1993. Review of Available Russian Literature Relating to Hydrogen Sulphide Decomposition in a Microwave/Radio-frequency Plasma. AECL Report RC-905.

Luinstra, E.A., R.S. Czura and P.M. Davies. 1993. Cold Plasma Decomposition of Hydrogen Sulfide. Shell Canada Limited.

Microwave-Initiated Decomposition of Hydrogen Sulphide[1]

UNIVERSITY OF ALBERTA, EDMONTON

The process of microwave-initiated catalysis (mwic) was invented by Dr. J.K.S. Wan at Queen's University in the early 1980s, and was applied successfully to the decomposition of hydrocarbons. Mwic entails using a catalyst (capable of catalyzing the desired reaction), which is heated by microwave pulses. In the "microwave off" period, the substance to be decomposed is adsorbed on the catalyst surface, and decomposes and desorbs in the "on" period. Employing a metal base catalyst, the process appears to function well with methane and other hydrocarbons.

It was hypothesized that when hydrogen sulphide (H_2S) is subjected to mwic, it may undergo either or both of the following reactions:

$$H_2S \xrightarrow[\text{catalyst}]{\text{mwic}} H_2 + \text{sulphur} \qquad (1)$$

and

$$H_2S \xrightarrow[\text{catalyst}]{\text{mwic}} H_2 + MS \qquad (2)$$

When researchers at the University of Alberta used a nickel-containing catalyst that was reported to be the catalyst of choice for mwic, it was found that both reactions (1) and (2) took place. Reaction (2) occurred readily, but reaction (1), which is the desired one, was much less significant.

Consequently, other metal catalysts were used under mwic conditions, but no decomposition of H_2S could be detected for most. Eventually, one catalyst heated by microwave energy to an apparent temperature of 1 200°C produced a 35.6 per cent conversion of H_2S to hydrogen in a single pass, but H_2S reacted with the catalyst, giving erratic results.

A new quartz reactor was designed so that a microwave absorber in a separate chamber could be used to heat the reactor for decomposing H_2S. In this arrangement, microwave energy interacting with the absorber generated sufficient heat to cause thermal decomposition of H_2S as it passed over alumina. A maximum decomposition rate of 41 per cent was achieved at ~1 200°C. It was hypothesized that conversion rates as high as 50 per cent could be achieved at higher temperatures. Proving this will be the subject of a new project to begin next year.

Publications

Strausz, O.P. 1993. Microwave-Initiated Decomposition of Hydrogen Sulphide. Final Report. April 1, 1992 - March 31, 1993. University of Alberta.

Strausz, O.P. 1992a. Microwave-Initiated Decomposition of Hydrogen Sulfide. April 1 - June 30, 1992. University of Alberta.

Strausz, O.P. 1992b. Microwave-Initiated Decomposition of Hydrogen Sulfide. July 1 - September 30, 1992. University of Alberta.

Strausz, O.P. 1992c. Microwave-Initiated Decomposition of Hydrogen Sulfide. October 1 - December 15, 1992. University of Alberta.

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[1] Funding was provided by Canadian Occidental Petroleum Ltd. and the Alberta Department of Energy.

Electrolysis of H_2S in Alkaline Solution[1]

SHELL CANADA LIMITED (CALGARY) AND
CANADA MINERAL ENERGY
TECHNNOLOGY(CANMET) (DEVON)

Although the heat of formation for hydrogen sulphide (H_2S) is much lower than that for water, the development of a commercial process for electrolyzing H_2S has proven elusive. While researchers have investigated electrolysis of liquid H_2S and H_2S in aqueous solution, all these potential processes are hampered by various technical difficulties.

Aqueous electrolysis appears to have some advantages, and is the subject of this project. The principal difficulties reported in the literature include: blocking of the anode with deposited sulphur; reduction of polysulphide (to sulphide) at the cathode in electrolytes having high polysulphide rank; and formation of by-products, such as thiosulphate, at high pH conditions.

The principal initial reaction at the anode, in which sulphur is formed, is believed to be as follows:

$$HS^- + OH^- \rightarrow 2e^- + H_2O + S$$

The sulphur, will dissolve in the alkaline medium to form polysulphide ions:

$$S + HS^-_{(x-1)} \rightarrow HS_x^-$$

It is also possible that the polysulphide ions form directly at the anode:

$$2HS^- + OH^- \rightarrow 2e^- + H_2O + HS_2^-$$

As electrolysis proceeds, the value of x increases. Eventually, the solution becomes saturated in sulphur, and sulphur appears at the anode. The value of x may approach five at this point, although this depends on pH and other factors.

At the cathode, reduction of water takes place to form hydrogen:

$$2H_2O + 2e^- \rightarrow H_2 + 2OH^-$$

Also at the cathode, an undesirable side reaction can take place that involves reduction of the polysulphide ion. This causes the appearance of HS^- at the expense of electrical power and sulphur production. Reduction of polysulphide can be prevented by installing a membrane and creating separate anode and cathode compartments. The membrane can be expensive, however. Furthermore, separating the electrodes complicates the chemistry, since pH shifts can occur, in opposite directions, in the anolyte and catholyte.

In the course of reviewing the literature on hydrogen technology and electrolysis, a possible solution to the difficulties cited above became apparent. This course of investigation, however, required electrochemical characterization of H_2S in certain solutions to determine the sequence of electron transfer and chemical reactions occurring at or near electrode surfaces. Then detailed electrolysis studies were carried out. Two different reactor designs were used: a single-compartment unit and one having two separate compartments.

It was found that the effectiveness of the electrolytic process in the single-compartment reactor was affected by parasitic reactions on the cathode side. Consequently, the product current efficiency decayed. The quality of the recovered sulphur was high, but H_2S gas was present in the recovered hydrogen.

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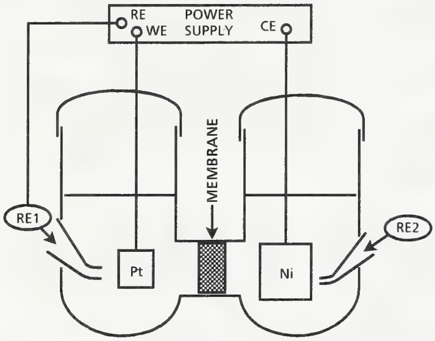
[1] Funding was provided by Shell Canada Limited, CANMET and the Alberta Department of Energy.

When the divided-compartment reactor was used, nearly ideal current efficiencies (>90 per cent) were achieved and excellent current densities higher than 0.5 Amperes per square centimeter were measured. Unhindered, continuous operation for up to 60 hours was possible, and anode blocking by sulphur was not observed.

The project will continue next year.

Divided (membrane) Cell



(Source: CANMET)

Schematic of divided-compartment reactor.

Publications

Petrovic, S., P. Komorowski, K. Michaelian, C.K. Preston, J. Szynkarczuk, S. Thind, R. Willier, J. Donini and E.A. Luinstra. 1993. Electrolysis of H_2S in Alkaline Solutions. Division Report WRC 93-01 (CF). CANMET.

Petrovic, S., P. Komorowski, K.H. Michaelian, J. Szynkarczuk, S. Thind, R. Willier and J. Donini. 1992. Electrolysis of H_2S in Alkaline Solutions. Division Report WRC 92-00 (CF). CANMET.

Petrovic, S., P. Komorowski, K.H. Michaelian, J. Szynkarczuk, S. Thind, R. Willier, J. Donini and E. Luinstra. 1992. Electrolysis of H_2S in Alkaline Solutions. Third Quarter Report. October 1 - December 3, 1992. Shell Canada Limited.

Hydrogen Sulphide Decomposition Using Modified Aluminas[1]

ALBERTA RESEARCH COUNCIL, DEVON

Studies have amply shown that γ-alumina catalyzes the thermal decomposition of hydrogen sulphide (H_2S) at elevated temperatures (>500°C). Transition metal sulphides have also been demonstrated to have catalytic activity for this process. The origin of the catalytic activity of alumina for H_2S decomposition is unknown, although the mechanism has been the subject of some investigation and speculation.

Thus far, most studies of H_2S decomposition have emphasized reactor designs, process conditions and, in particular, product separation. While it is true that separation of hydrogen and sulphur will be an extremely important part of any such process, it is also necessary to recognize that thermal efficiency, catalyst turnover frequency (rate of achieving equilibrium) and lifetime will also be key factors in determining the economic viability of any process. It is for these reasons that the intrinsic properties of the catalysts are being examined as a separate issue in this project.

Aluminas occur in a number of crystalline phases, of which the two most important, catalytically, are γ- and η-aluminas. These two forms of alumina are stable to moderately high temperatures, but can undergo a series of thermally induced phase transformations, ultimately producing α-alumina.

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[1] The project was funded by Alberta Research Council and the Alberta Department of Energy.

$$\gamma\text{-}Al_2O_3 \xrightarrow{730^\circ C} \delta\text{-}Al_2O_3 \xrightarrow{1000^\circ C} \theta+\alpha\text{-}Al_2O_3 \xrightarrow{1200^\circ C} \alpha\text{-}Al_2O_3$$

$$\eta\text{-}Al_2O_3 \xrightarrow{850^\circ C} \theta\text{-}Al_2O_3 \xrightarrow{1200^\circ C} \alpha\text{-}Al_2O_3$$

The surfaces of both aluminas are covered with a layer of hydroxyl groups of five distinct types. Thermal dehydroxylation of these surfaces produces pairs of Lewis acid and base sites.

$$Al\text{-}OH + Al\text{-}OH \rightarrow H_2O + \underset{\text{Lewis base}}{Al\text{-}O^-} + \underset{\text{Lewis acid}}{Al^+}$$

Dehydroxylation below 400°C produces relatively weak Lewis sites which have no catalytic activity. Above 400°C, a new and stronger type of Lewis acid (and also Lewis base site) appears and increases in abundance up to dehydroxylation at 600°C.

At 500°C, a third and very strong type of Lewis acid site appears and increases in number density until dehydroxylation is complete at about 900°C. The density of these strongest Lewis sites is three times greater on η-alumina compared to γ-alumina under similar conditions.

The reports from previous studies show that pure alumina appears to have little or no activity for H_2S decomposition below 500°C, whereas aluminas promoted with transition metal sulphides (e.g., molybdenum sulphide (MoS_2) are more active at this temperature. These observations are certainly related to the relative activities of these catalysts. Published reports also indicate that electron-donating sites are important for H_2S decomposition on MoS_2. On an alumina surface, the electron-donating sites are $Al\text{-}O^-$ sites, and the adsorption of H_2S on such a site would lead to relatively strong S-O bonds. This would inhibit the subsequent desorption of sulphur. However, the lower level of activity for alumina is probably related to the expected low concentration of strong Lewis sites which are undoubtedly involved in the catalytic process.

H_2S is known to adsorb coordinatively on alumina in two distinct forms, with two corresponding desorption temperatures (ca. 130°C and 290°C). Both forms of coordinated H_2S increase in concentration as the activation temperature of alumina increases up to 500°C. Thereafter, it decreases with increasing temperature of activation. The sites for these non-dissociated forms of H_2S are probably the weaker Lewis acid sites.

$$Al^+ + H_2S \rightleftharpoons Al^+{:}SH_2$$

It is also known that adsorption of H_2S at 25°C on an activated alumina, which has strong Lewis sites, can result in dissociation:

$$Al^+ + AlO^- + H_2S \rightarrow Al\text{-}SH + Al\text{-}OH$$

It is probable that both dissociative and non-dissociative adsorption of H_2S occur at the temperatures used for H_2S decomposition, but whether either or both are key steps and what occurs subsequently can only be speculated.

The strength and number of Lewis acid and base sites can be changed by the addition of promoters and selective poisons. In the present context, it is required that these additives be stable at the reaction temperatures for H_2S decomposition. The strengths of acidic sites can be increased by fluoridation or chlorination, while basic sites can be enhanced by the addition of alkali metal oxides. By varying the strength and availability of these Lewis sites, it is possible to explain the mechanism and the important properties of alumina that are involved in the catalytic decomposition of H_2S.

Experiments were carried out to determine the relative importance of Lewis acid and base sites on alumina in catalytic H_2S decomposition, and to determine whether this catalytic activity can be enhanced by chemical modification of the alumina.

To avoid prejudiced results, both η- and γ-aluminas were prepared from a single starting material to produce catalysts with the same amounts of minor impurities.

The catalysts were tested in a quartz tubular reactor to determine H_2S conversion (hydrogen production) as a function of residence time. Experiments at 600°C and 700°C showed that η-alumina had a higher catalytic activity, thus indicating that the acid or base strength was important.

The γ-alumina was modified to increase its acid strength and remove most basic sites by chlorinating the catalyst surface. In a second modification, the strongest acid sites were poisoned by adding sodium oxide, which left the basic sites untouched. It was found that the catalytic activity of the chlorinated alumina was higher than the sodium-treated alumina, but both were less active than the unmodified catalyst.

Finally, the γ-alumina was fluoridated to increase its acidity. The activity of this catalyst was found to be even lower than the sodium-treated catalyst.

It was concluded that the best catalyst may be an alumina possessing both acid and base sites that are moderately strong.

Publications

McFarlane, R.A. 1992a. Hydrogen Sulphide Decomposition Using Modified Aluminas. First Quarter Report. Alberta Research Council.

McFarlane, R.A. 1992b. Hydrogen Sulphide Decomposition Using Modified Aluminas. Second Quarter Report. Alberta Research Council.

McFarlane, R.A. 1992c. Hydrogen Sulphide Decomposition Using Modified Aluminas. Third Quarter Report. Alberta Research Council.

McFarlane, R.A. 1992d. Hydrogen Sulphide Decomposition Using Modified Aluminas. Final Report. Alberta Research Council.

McFarlane, R.A. and R. Zacharkiw. 1993. Decomposition of Hydrogen Sulphide Using Modified Aluminas. Alberta Research Council.

Hydrogen Separation

Separation of produced hydrogen from unreacted feedstock or reaction by-products an important aspect of the Alberta Hydrogen Research Program.

Although several straightforward hydrogen separation methods exist, using these technologies in combination with thermally or chemically energized hydrogen-production processes is often inefficient. This inefficiency is frequently caused by large changes in the process temperature and pressure.

In addition, some existing hydrogen-producing processes might become economically attractive if they could be combined with suitable separation methods.

For these reasons, three hydrogen separation projects have been initiated. One was completed earlier and the other two are described in the following section.

High-Temperature Separation of Hydrogen Using Novel Ceramic Membranes[1]

ALBERTA RESEARCH COUNCIL, DEVON

Gas separation using thin-film polymeric materials offers significant economic advantages over conventional separation processes, but these polymeric membranes are not suitable for the high-temperature applications that are likely to be used in any new or improved hydrogen-production process in Alberta.

A possible alternative is ceramic membranes based on porous metal oxides, such as alumina, silica, titania and zirconia, and titania/alumina and zeolite/sol composites. Compared with polymeric membranes, they offer higher thermal stability (>1 000°C versus <200°C), lower pressure drop, longer life and better permeability. They are 10 times more expensive, however.

Separation of gases at high temperature can result in substantial energy savings. Preferential removal of one of the reactants by a ceramic membrane capable of withstanding high temperatures can result in conversions well above those attainable at the temperature dictated by the reaction equilibrium in a conventional reactor.

A project to develop novel ceramic membranes for high-temperature separation (up to 1 000°C) of hydrogen began in 1990. The research objectives are: (1) to optimize the membrane-preparation technique by the sol gel route, as well as by alumina sol, zeolite sol, titania (Ti) and titania/alumina (Ti/Al) composite membranes; and (2) obtain performance data for the tubes coated with these membranes. Also included is the preparation and characterization of zirconia-based membranes.
The techniques developed in this project can possibly result in membranes with an average pore size <2 nanometer (nm), which are capable of providing a high selectivity for hydrogen separation.

The recipes developed were used to prepare membrane-coated alumina support tubes. The zeolite/sol and Ti/Al membranes were tested up to 750°C, while the Ti membrane was tested up to 1 000°C. All were found to be thermally stable up to the maximum operating temperatures used in the tests, as shown by the reproducible results obtained after extensive temperature cycling.

Generally, the separation factors for the pairs H_2/CH_4, H_2/CO_2, H_2/CO, H_2S/CO_2, and H_2/H_2S (below 400°C, under non-reacting conditions) were approximately 50 per cent of their respective Knudsen (theoretical) values. The membrane performance was ranked as follows:

Ti > Ti/Al (33 per cent titania) > zeolite > alumina >> ASTD5[2]

Zeolite membranes with different concentrations of zeolite on the surface were prepared. The separation factors were found to be more or less independent of the surface concentration of zeolite concentration. The results from separating a n-hexane from 2,2-dimethylbutane system on the zeolite-coated membrane showed no molecular sieving effect for molecules that corresponded in size to C_6 hydrocarbons.

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[1] Funding was provided by Shell Canada Limited, Alberta Research Council and the Alberta Department of Energy.

[2] ASTD5 (Alicoa Separation Technology Division 5nm) ceramic tube supplied by U.S. Filters.

The results of the study using Ti-coated tubes for the hydrogen/hydrogen sulphide (H_2/H_2S) system showed that the separation factor under non-reacting conditions (below 400°C) was approximately 48 per cent of the Knudsen value. The study at 1 000°C shows there is substantial decomposition of H_2S and the conversions obtained were well above those dictated by the reaction equilibrium. However, the effect of separation alone on the conversions could not be discerned owing to the location of the heater element within the reaction mixture, which interacted with the H_2S environment at high temperature. In addition, the Ti membrane also interacted with the system at such elevated temperatures.

A composite membrane of Ti/Al (33 per cent Ti) prepared in this study was shown to give the desired synergy, having the good porosity of alumina and the thermal stability of Ti. For economic reasons, optimizing the Ti composition in this type of composite membrane is recommended for future work.

Publications

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Rangwala, H.A. and L. Johanson. 1992. High Temperature Separation of Hydrogen Using Novel Ceramic Membranes. Final Report (1991-1992). Alberta Research Council.

Smith, K.J. and L. Johanson. 1991a. Development of Ceramic Membranes for High Temperature Separation of Hydrogen. A Review. Alberta Research Council.

Smith, K.J. and L. Johanson. 1991b. High Temperature Separation of Hydrogen Using Novel Ceramic Membranes. Final Report (1990-1991). Alberta Research Council.

High-Efficiency Hydrogen Separation and Production[1]

HIGHQUEST ENGINEERING INC., VANCOUVER

While Alberta companies are capable of producing more hydrogen than is currently needed in the province, the demand for hydrogen in other locations exceeds the ability to produce it. One way to satisfy this demand is to build more hydrogen-production facilities. Another is to make the current facilities more efficient.

The latter option is being explored by Highquest Engineering, which has developed novel gas-separation technologies that are applicable to various gas mixtures. In this project, Highquest is developing a system capable of improving the yield and purity of hydrogen from steam-methane reformers and recovering hydrogen from "lean" (low-BTU) hydrogen streams where the hydrogen concentration is at least 20 per cent.

The Highquest technology is based on Pressure Swing Adsorption (PSA). In its conventional mode, PSA has a number of advantages, but it cannot be used to recover hydrogen economically from lean streams owing to performance limitations and high compression energy requirements. Highquest, however, has developed a proprietary variant called Thermally Coupled Pressure Swing Adsorption (TCPSA) which combines the normal pressure swings of PSA with energy recovery. This results in exceptional energy efficiency. For example, TCPSA can be used to split a syngas stream into three fractions: high-purity hydrogen; high-purity carbon dioxide; and a recycle stream rich in carbon monoxide (CO) and methane.

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[1] Funding was provided by Highquest Engineering Inc., NORAM Engineering and Constructors Ltd., B.C. Ministry of Advanced Education, Training and Technology, Canadian Fusion Fuels Technology Project (Ontario Hydro), Alberta Oil Sands Technology and Research Authority, and the Alberta Department of Energy.

The ability to obtain a compressed carbon dioxide (CO_2) by-product and to return a CO-rich stream to a syngas generator contributes to the overall efficiency of hydrogen production.

Unlike conventional PSA cycles, TCPSA can achieve very high recovery (up to 99 per cent) of high-purity hydrogen from concentrated streams, such as high-BTU syngas. Recent tests showed that TCPSA readily obtains moderately high recovery (90 per cent) of high-purity hydrogen from low-concentration (e.g., 30 per cent hydrogen) fuel gas, which could not be processed by conventional PSA.

During the past year, Highquest has been collaborating with NORAM Engineers and Constructors Ltd. to design pilot- and full-scale industrial modules. The scaleup engineering was supported by computer modelling and bench-scale tests. The pilot plant is being developed for demonstration in 1994 at a refinery site in Alberta.

Publication

Keefer, B.G. 1993. TCPSA Pilot Plant Demonstration Program. Phase A Report. Highquest Engineering Inc.

Hydrogen Use

Although oil refining and synthetic crude oil production rank among the largest uses of hydrogen in Alberta, even greater quantities are used by fertilizer and methanol producers. Hydrogen is also used in manufacturing chemicals and pharmaceuticals, and is important in steel making and metallurgy. Thus, the Alberta Hydrogen Research Program encompasses all possible uses for hydrogen in the province, with equal emphasis on improving the efficiency of current hydrogen-consuming processes and finding new uses for hydrogen in Alberta.

Six research projects related to this aspect of the program were under way during 1992/93.

Hydrogen Utilization in Bitumen Upgrading[1]

ALBERTA CHAMBER OF RESOURCES, EDMONTON

The use of hydrogen as a process gas constitutes a major expense in bitumen upgrading. While the net total amount of hydrogen that is added can be determined, the details of the mechanisms by which the process hydrogen is incorporated into the products are less well known.

The objective of this study was to trace experimentally the transfer of hydrogen from the gas phase to the hydrogenated bitumen products during both primary and secondary hydroprocessing to synthetic crude oil.

Specialized equipment and services were provided by the Energy Research Laboratories of the Canada Centre for Mineral and Energy Technology (CANMET) near Ottawa. Direction was provided by the Oil Sands Task Force of the Alberta Chamber of Resources.

Tracing the hydrogen transfer was achieved by using the non-radioactive isotope of hydrogen (deuterium) as the process gas. The deutero-species in the gas products were measured by mass spectroscopy. The molecular distribution of deuterium within the liquid products was determined by 1- and 2-dimensional nuclear magnetic resonance (NMR) spectroscopic techniques.

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[1] Funding was provided by the Alberta Chamber of Resources, CANMET and the Alberta Department of Energy.

NMR spectroscopy is well suited to the identification of chemical functional groups in hydroprocessed products. Analyses of fuels using hydrogen and carbon-13 Nuclear Magnetic Resonance (^{1}H and ^{13}C NMR) have become widespread. For example, the aromatic contents of petroleum processing products are frequently measured as NMR-derived aromaticities.

Deuterium is also an "NMR active" nucleus. Consequently, deuterium NMR can be used to characterize the deutero-species created when hydroprocessing with deuterium gas.

A series of hydrocracked products was generated using Athabasca bitumen feedstock. The runs were performed in a continuous-flow bench-scale unit. Two sets of conditions were chosen to generate both low- and high-pitch conversion products. The process gas was hydrogen. The same sets of conditions were then used to hydrocrack the bitumen using deuterium (called deuterocracking) as the process gas. The liquid products generated by these four runs were distilled using the ASTM D1160 (American Standard Testing Methods, Designation 1160) method.

Secondary hydroprocessing was then performed on the light gas oil (LGO) and heavy gas oil (HGO) from deuterocracking. The LGO and HGO fractions of the low- and high-severity runs using deuterium were hydrotreated in a microreactor. Hydrogen was used as the process gas. The hydrotreated products were fractionated by spinning-band distillation.

When the gases produced from deuterocracking were analyzed, all samples at both the low-severity and high-severity conditions were found to contain significant amounts of HD and H_2. This indicated that hydrogen was released from the feedstock.

The 1- and 2-dimensional NMR spectra for carbon, hydrogen and deuterium in the hydrocracked and hydrotreated products were collected. A comparison of the NMR data for hydrogen- and deuterium-hydrocracked products identified which chemical species were deuterated during hydrocracking. The differences in products generated under low- and high-severity hydrocracking were compared. During primary upgrading, deuterium was found to be incorporated into all products, including pitch, as well as most chemical functional groups. The incorporation of deuterium was increased at high severity (~85 per cent pitch conversion) compared with that at low severity (~64 per cent pitch conversion). The distributions of proton and deuteron functional groups were similar, suggesting that the reaction pathways followed at low and high severity are similar. The high-severity LGO, HGO and pitch had higher aromaticity values than the corresponding low-severity products, as determined by ^{13}C NMR. This suggested that the high-severity products have higher polyaromatic contents and are lower quality.

The synergism between hydrocracking and hydrotreating was studied by determining which of the chemical species deuterated during hydrocracking were altered by hydrotreating. This was achieved by comparing the NMR data of the deuterium-hydrocracked LGO and HGO with those of their hydrogen-hydrotreated products. These results were used to develop a model of the chemical hydrogenation pathways involved in primary and secondary hydroprocessing.

This information will be useful to industry for planning additional Research & Development aimed at optimizing the use of hydrogen in bitumen upgrading.

Publications

Dettman, H.D. and D.J. Patmore. 1992. Hydrogen Utilization in Bitumen Upgrading: An Experimental Study of the Fate of Process Hydrogen. Second Quarter Report. CANMET.

Dettman, H.D. and D.J. Patmore. 1991. Hydrogen Utilization in Bitumen Upgrading: An Experimental Study of the Fate of Process Hydrogen. First Quarter Report. CANMET.

Dettman, H.D., D.J. Patmore and S.H. Ng. 1993a. Hydrogen Utilization in Bitumen Upgrading - Final Report. CANMET.

Dettman, H.D., D.J. Patmore and S.H. Ng. 1993b. The Fate of Process Hydrogen in Bitumen Upgrading. In: "Proceedings of Oil Sands: Our Petroleum Future", Edmonton, April 4 - 7, 1993.

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Multi-stage Hydrocracking of Athabasca Bitumen and Cracked Products[1]

SYNCRUDE CANADA LTD., EDMONTON

When Athabasca bitumen is heated in a nitrogen atmosphere under cracking conditions, large amounts of carbonaceous solids (coke) are formed. If the atmosphere is changed to hydrogen, the formation of carbonaceous solids is suppressed and nearly eliminated at high hydrogen partial pressures.

Reports in the literature suggest that coke formation is prevented by a simple mechanism of hydrogen transfer to the radical intermediates, which would likely produce a distillate molecule and a lower molecular weight residuum molecule. This mechanism suggests that in the presence of hydrogen, the rate of conversion of residuum would be slower than in its absence. If a tracer were used, it would be incorporated into the residuum, and hydrocarbon gases would be formed from the fragmentation of side chains produced during the initial carbon-breaking process. Experimental data, however, suggest that none of the above postulates is true.

The rate of conversion of Athabasca bitumen residuum is the same in the presence or absence of hydrogen, and tracers in the hydrogen are not incorporated into the residuum fraction during cracking. Neither gas nor coke is formed in what is believed to be the side-chain cracking step. Gases appear to be formed from hydroaromatic structures.

To gain a better understanding of the decomposition mechanism, a series of cracking experiments on Athabasca bitumen residuum was carried out at 400°C under either nitrogen (coking) or hydrogen (hydrocracking) atmospheres, and then the liquid, gaseous and solid products were compared.

The yield of reactor solids was considerably lower in the hydrocracking case, and gas yield increased significantly. The yield of distillates also rose. Analysis of the gaseous products showed that the composition of the gases was not influenced by the presence of hydrogen and it did not affect the relative rates of residuum conversion.

It was postulated that during the first 40-50 per cent conversion of the residuum, the reaction involves the cleavage of side chains. This produces mainly distillate, with little production of gases and solids.

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[1] The project is being funded by Syncrude Canada Ltd. and the Alberta Department of Energy.

Subsequent conversion is thought to involve carbon-to-carbon bond breaking in hydroaromatic rings to give an aliphatic-carbon radical. This radical undergoes fragmentation to produce gases and distillate. Another radical is then produced: an aromatic-carbon type that cannot fragment readily. In the coking case, the aromatic-carbon radical likely condenses with a similar radical in reactions that will eventually produce coke. In the presence of hydrogen, it is proposed that the aromatic-carbon radical reacts with hydrogen to give a carbon-to-carbon bond and a hydrogen radical which attacks an aromatic ring. This leads to decomposition of the aromatic molecules, producing gases and distillate.

Using this postulated mechanism as a guide, further experiments were carried out to determine the effects of temperature, pressure and time on bitumen conversion. Then, a series of experiments was conducted to determine how bitumen hydrotreating before coking or hydrocracking would affect the products. At year-end, the results of this work were being analyzed.

The project will continue.

Publications

Sanford, E.C. 1993a. Mechanism of Coke Prevention by Hydrogen During Residuum Hydrocracking. 205th National Meeting, American Chemical Society, Denver CO, March 28 - April 2, 1993.

Sanford, E.C. 1993b. Multistage Hydrocracking of Athabasca Bitumen and Cracked Products. Fourth Quarter Progress Report. January - March 1993. Syncrude Canada Ltd.

Sanford, E.C. 1992a. Catalyst Selectivity During Hydrocracking: The Effect of Temperature, Pressure and Time on Bitumen Conversion and Catalyst Deactivation in a Batch Stirred Tank Reactor. First Quarter Report. April - June 1992. Syncrude Canada Ltd.

Sanford, E.C. 1992b. A Molecular Approach to Understanding Residuum Conversion During Coking, Hydrocracking and Hydrogenolysis Hydrocracking of Athabasca Bitumen Over a Wide Range of Conversions. Syncrude Canada Ltd.

Sanford, E.C. 1992c. Influence of Hydrogen and Catalyst on the Removal of Heteroatoms, Aromatics and CCR During Cracking of Athabasca Bitumen Residuum Over a Wide Range of Conversions. Syncrude Canada Ltd.

Hydrogen Optimization Study[1]

ALBERTA CHAMBER OF RESOURCES, EDMONTON

One of the original premises of the Alberta Hydrogen Research Program was that Canada will need more crude oil from non-conventional sources, such as the oil sands, as reserves of conventional light and medium crude oils decline. In turn, this will create a greater demand for hydrogen, which is used to upgrade synthetic crude oils to refinery-acceptable feedstocks. To keep the costs of upgrading as low as possible, it is necessary to make the current methods of using hydrogen more cost-efficient, or find new or improved ways of using hydrogen.

Thus, in a project coordinated by the Oil Sands Task Force of the Alberta Chamber of Resources, and carried out last year by RTM Engineering Ltd. (now RTM Energy Division of Stanley Industrial Consultants Ltd.), the objective was to review and then select new or emerging technologies that have demonstrated some promise for improving the use of hydrogen in upgraders and refineries. The project also updated the hydrogen inventory study completed in 1988.

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[1] Funded jointly by Alberta Chamber of Resources, CANMET and the Alberta Department of Energy.

For purposes of this project, it was assumed that 15 800 cubic meters per day of Cold Lake bitumen would be processed in a new upgrader located near Fort Saskatchewan and Redwater, with startup in the year 2000. This upgrader was treated as either a stand-alone unit or one that operated in conjunction with a refinery producing motor gasoline, jet fuel and diesel fuel. The actual refinery products were those projected to be in demand in the year 2000.

Taking into consideration environmental and market factors likely to prevail in the year 2000, a combination upgrader/refinery was considered to be the best option. It would:

- eliminate duplication of hydrogen processing units for naphtha, jet fuel, diesel fuel and gas oil;
- provide common hydrogen production and recovery facilities;
- avoid the necessity for crude distillation occurring at a separate refinery;
- allow residual products from refining to be converted in the upgrader; and
- provide other synergistic benefits for upgrading and refining.

During 1992/93, a second phase of this project was carried out. Its objective was to assess certain refinements that might be included in the upgrader. These included the following:

- replacing natural gas hydrogen-production units with a multi-unit complex to produce hydrogen for bitumen upgrading and incremental production of liquid fuels, and/or incremental synthetic crude oil (SCO) from natural gas;
- producing finished refined products in the upgrader, as well as SCO; and
- combining the above concepts to provide maximum synergy and significantly improve upgrader economics.

Each of these aspects was assessed, and the study results are available from the Alberta Chamber of Resources for a nominal fee.

Publications

McCann, T.J. 1993. Upgrader Optimization Study. Phase 2 Report. Prepared for Alberta Chamber of Resources. Stanley Industrial Consultants Ltd.

McCann, T.J. 1991a. Optimum Hydrogen Use in Upgrading and Refining. Phase I Report. Prepared for Oil Sand Task Force, Alberta Chamber of Resources. RTM Engineering Ltd.

McCann, T.J. 1991b. Optimum Hydrogen Use in Upgrading and Refining. Prepared for Oil Sand Task Force, Alberta Chamber of Resources. RTM Engineering Ltd.

Wide-Cut Cold Lake Blend Distillate Hydrotreating Study[1]

IMPERIAL OIL RESOURCES LIMITED, CALGARY

The development of oil sands reserves is partly constrained by the ability of refiners to process economically the high-sulphur, high-viscosity bitumen that is common to the Athabasca and Cold Lake deposits. Consequently, an effort has been under way for several years to develop new products from bitumen to enable more of the reserves to be developed. This project represents one approach, and involves increasing the hydrogen-to-carbon ratio by hydrotreating a wide-cut (~100°-500°C) distillate stream.

The objective was to use "partial upgrading" on Cold Lake Blend, a mixture of approximately 70 per cent bitumen and 30 per cent natural gas condensate.

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[1] Funding was provided by Imperial Oil Resources Limited and the Alberta Department of Energy.

This process could separate the Cold Lake Blend into two streams: a "vacuum resid" and an "overheads distillate". Instead of using conventional high-severity upgrading of the resid, the bottoms would be emulsified so the product could be used as a fuel for large energy consumers, such as utility companies. The overheads stream would be hydrotreated under moderate conditions to remove sulphur and nitrogen and to improve the catalytic cracking characteristics. The hydrotreated overheads stream could be marketed as a replacement for conventional light, sweet crude.

This approach differs from conventional upgrading in three aspects. First, it does not attempt to convert vacuum resid into a feedstock for a conventional refinery. Second, it is substantially less expensive, and third, it can be undertaken on a relatively small scale.

Wide-cut distillate hydrotreating is a critical component within the wider partial upgrading work that is under way at Imperial Oil Resources Limited. For the entire project to be economically viable, the expected improvements in desulphurization, denitrogenation and catalytic cracking must occur, making hydrotreating a pivotal aspect.

The project was designed to assess the performance of a wide-cut distillate hydrotreating step. This included determining the product quality and catalyst run length. A 90-day run was conducted to assess the catalyst activity using a commercially available catalyst with the 120-510°C fraction of virgin Cold Lake Blend. The operating conditions were within the regime of current distillate and gas oil hydrotreating. Most of the run was conducted at a base liquid hourly space velocity (LHSV), but part of the run was conducted at half this level.

Frequent spot samples were analyzed for sulphur and aromatics during the test to assess the performance and to adjust the operating conditions. Periodically, samples were analyzed for nitrogen content and hydrogen consumption. All liquid product was retained for detailed fraction analyses.

At the base LHSV, analyses indicated desulphurization and denitrogenation levels of approximately 97 per cent and 85 per cent, respectively. These figures increased to 99 per cent and 97 per cent, respectively, at half the base rate. No significant change occurred in the desulphurization level throughout the run, showing good maintenance of catalyst activity for hydrodesulphurization. The level of denitrogenation at the end of the run had decreased to approximately 81 per cent, indicating some catalyst deactivation for the hydrodenitrogenation reactions. The product aromaticity showed a gradual increase during the run, also indicating that some catalyst deactivation had occurred. Infrared analysis showed that the level of aromatics saturation was in the 9-12 per cent range.

Comparison of the feed and product streams showed that the quality of the jet fuel cut was not affected, as measured by smoke point. The diesel fuel cut showed a cetane index of 44.5 at the base LHSV and 46.7 at half the base LHSV, indicating a significant improvement over the feed diesel cetane index of 40.9. The aromatics level of the "cat feed" was reduced by 23-32 per cent.

Overall, the project results were promising, especially for the development of a small-scale process for bitumen upgrading.

Publication

Ghosh, M., S.E. McGregor, C.A. Swift, A. Ravella and D.W. Kraemer. 1992. Wide-Cut Cold Lake Blend Hydrotreating Study. Imperial Oil Resources Ltd.

Hydrogen Peroxide by Direct Oxidation of Hydrogen[1]

ALBCHEM INDUSTRIES LTD., EDMONTON

Following the recent development in Alberta of a unique laboratory procedure to make hydrogen peroxide (H_2O_2) directly from hydrogen, Albchem Industries of Edmonton has begun a project to scale up the manufacturing process.

The laboratory procedure, which involves direct oxidation of hydrogen over a catalyst, was developed by Dr. K.T. Chuang of the University of Alberta. A patent application has been filed for the process. By comparison with the conventional, two-step process for making H_2O_2, the "Chuang Process" is simpler and the laboratory results suggest that it can produce hydrogen peroxide at half the cost. Furthermore, the Chuang Process avoids the production of organic effluents, which are by-products of the conventional method.

Because the project began late in the year, some planned activities have been delayed. Nonetheless, a test reactor for conducting larger scale production of H_2O_2 has been purchased and was being modified at year-end. An agreement has been reached to carry out experiments at the Praxair Canada gas bottling facility in Edmonton, where the feed gas is readily available. Albchem has begun producing the catalyst in quantities sufficient to carry out the experiments.

There are both economic and environmental reasons behind this project. Hydrogen peroxide is becoming an increasingly important commodity in Alberta and other locations where an active pulp and paper industry exists. The chemical is being used as a bleaching agent in place of, or as a supplement to, chlorine, which has been linked to the formation of dioxins that are found in the effluents from pulp and paper mills. Potentially, the surplus hydrogen, produced by Albchem during the manufacture of sodium chlorate, could generate 25 000 tonnes a year of H_2O_2. Recent sales of H_2O_2 have been rising by nearly 10 per cent annually in North America.

The project will continue next year.

Special Projects

The Alberta Hydrogen Research Program encourages research on all aspects of hydrogen that are of interest to industry. Four projects under way in 1992/93 that did not fall within the previous subsections of this report, but are supported by industry, are described below.

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[1] The project is being funded by Albchem Industries Ltd., Praxair Canada and the Alberta Department of Energy.

Japan-Canada Hydro-Hydrogen Pre-feasibility Study[1]

HYDROGEN INDUSTRY COUNCIL, MONTREAL

The Japanese government is interested in developing a system for using renewable energy on a global scale, in which hydrogen is used as an energy medium. Because this concept aims to keep atmospheric emissions to a minimum, the Japanese government commissioned a study that focused on Canada's potential for generating power through hydroelectrical facilities. This power could be converted to hydrogen (H_2) via electrolysis of water and transported to Japan. Subsequently, representatives of Japanese industry approached various agencies in Canada.

The end result was a techno-economic analysis that focused on various supply options that would allow electrolytically produced hydrogen to be converted to other products for transport to Japan.

The alternatives considered were: liquid hydrogen (LH_2); methanol; ammonia; and methylcyclohexane, all of which could be used directly as fuels or be converted to hydrogen. The study also investigated Canada's ability to supply these carriers of power (called vectors). The study was financed jointly by Japanese and Canadian partners under the management of the Hydrogen Industry Council. The overall investigation was carried out by SNC Lavalin, with individual components being studied by Monenco AGRA Inc., The Electrolyser Corporation, Canadian Liquid Air Ltd., Econoden Inc. and CDS Research Ltd.

Large amounts of potential hydroelectric power were identified in Manitoba, Alberta and British Columbia. It was concluded that 1 000 MW of power would be available from northern Manitoba until the year 2005, while British Columbia could supply 300 MW. In a second phase, up to the year 2020, 3 000 MW would be available from northern Manitoba.

The power-supply scenarios selected as a basis for the study were for 1 000 MW and 4 000 MW systems, as follows:

LH_2

- produce gaseous hydrogen at the power source in Manitoba, and transport it by pipeline to a port in British Columbia, where it would be converted into LH_2 for transshipment to Japan; and
- transmit electricity by conventional transmission lines from a power source in Manitoba to British Columbia, where it would be used to produce gaseous hydrogen, which would then be liquefied for transshipment to Japan;

Methanol

- produce hydrogen at the power source, transport gaseous hydrogen and oxygen by pipelines to a coalmine site in Alberta, gasify coal in the presence of oxygen to produce synthesis gas, use the synthesis gas and hydrogen to make methanol, and transport the methanol by pipeline to British Columbia; and
- transmit power to a coalmine site in Alberta, where hydrogen, oxygen and synthesis gas are generated, produce methanol from synthesis gas and hydrogen, and transport the methanol by pipeline to British Columbia.

Ammonia

- produce hydrogen and ammonia at the power source and transport the ammonia by pipeline to British Columbia.

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[1] The project was funded equally by Japanese and Canadian parties. The Japanese funding was shared by Electric Power Development Co. Ltd., Iwatani International Corporation and Mitsui & Co. Ltd. The Canadian parties were: Natural Resources Canada, Alberta Department of Energy, British Columbia Ministry of Advanced Education, Trade and Technology, and Manitoba Department of Industry, Trade and Tourism.

Methyl Cyclohexane

- produce hydrogen at the power source, use the hydrogen to hydrogenate toluene and produce methylcyclohexane (MCH), transport the MCH by pipeline to British Columbia and ship it to Japan.

From the analysis of these various options, several conclusions were reached. For LH_2, it was recommended that electrolytic hydrogen be produced at the source of hydroelectric power in Manitoba, and gaseous hydrogen be transported by pipeline to a British Columbia port. At the port, the hydrogen would be liquefied for trans-Pacific shipping. It was estimated that this option would entail operating costs of $4.09/kg of liquefied hydrogen and would require a capital investment of $5.3 billion.

If the methanol vector were chosen, the recommended option would be to deliver electrical power by conventional transmission line from Manitoba to a coalmine location in Alberta, where the production of electrolytic hydrogen and oxygen would be integrated with a coal gasification operation. The resulting methanol would be transported by pipeline to the west coast. The estimated operating cost of this option was $0.37/kg, with a capital investment of $3.3 billion.

Publication

Hydrogen Industry Council. 1993. Japan-Canada Joint Techno-Economic Analysis for A Clean Energy Supply System Between Japan and Canada. Prepared for Hydrogen Industry Council and funding parties.

The University of Calgary Hydrogen Industry Chair

THE UNIVERSITY OF CALGARY, CALGARY

A position at The University of Calgary was established with a grant from the Alberta/Canada Energy Resources Research Fund (A/CERRF), some industry participants[1] and the Natural Sciences and Engineering Research Council of Canada.

The objective is to conduct hydrogen research that will be of direct benefit to the industry partners.

At year-end, applications for the chair position were being reviewed.

Resistance of Thermal Spray Coatings to Hydrogen Penetration

CENTRE FOR FRONTIER ENGINEERING RESEARCH, EDMONTON

Atomic hydrogen can enter steel and gather at various locations in the metal to cause blistering and cracking. Pressure vessels, pipelines and downhole piping are susceptible to this hydrogen-induced damage where high stresses, the availability of atomic hydrogen and distortion of the metallic lattice coincide.

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[1] Research funds contributed by A/CERRF in 1991 are being matched in subsequent years by the following group of industry participants: Shell Canada Limited, Esso Resources Canada Limited, Husky Oil, Gulf Canada Resources Ltd, AMOCO Canada Petroleum Company, TransAlta Utilities Corporation and Alberta Oil Sands Technology and Research Authority. Also, substantial funding is being provided by the Natural Sciences and Engineering Research Council of Canada.

Currently, hydrogen penetration is controlled by using stainless steels, exotic alloys and the application of inhibitors to the metal surface. The metal strength, hardness and microstructure can also be controlled, although some of these techniques are expensive.

An alternative, which is being investigated in this project, involves using thermal spray coatings to provide a barrier to hydrogen penetration. Already, such coatings have been used inside pressure vessels in Alberta, and have shown promise for use in this application.

In this phase of the project, there are two objectives:

- determine experimentally the effectiveness of several existing coatings in preventing hydrogen penetration in steel; and
- study the mechanism by which hydrogen penetrates the coating.

The general procedure was to measure the amount of hydrogen that passed through coated and uncoated specimens of steel, called "coupons." For a given type of steel, several coatings were examined. Certain coating characteristics were also studied. These included porosity, thickness distribution and resistance to general and pitting corrosion.

Since the project started late in the year, only limited results are available thus far.

A literature review was completed and ASTM A516 Grade 70 steel was obtained for use as the base material. Three coating methods were chosen: combustion, plasma and High Velocity Oxy Fuel (HVOF). Using these methods, several different alloys were applied as coatings. They include iron-based and nickel-based materials.

At year-end, testing of the coated specimens had begun.

The project will continue next year.

Funding was provided by Shell Canada Limited, Syncrude Canada Ltd., Sherritt Technologies and the Alberta Department of Energy.

Hydrogen Research Program Workshop

INFO-TECH CONFERENCE MANAGEMENT,
CALGARY

On October 8, 1992, the Alberta Department of Energy sponsored a one-day workshop on hydrogen research projects funded by the department and industry. This was the fifth such workshop. Fourteen presentations, including one by a guest speaker from Argonne National Laboratories, were made to an audience of 50 attendees.

Based on an enthusiastic response by those who attended, another similar conference is planned for 1993.

Titles of the conference presentations are listed below.

Alternative Hydrogen Production

A Claus Plant Modification for Hydrogen Production

Cold Plasma Decomposition of Hydrogen Sulphide

The CO-Catalyzed Conversion of H_2S to H_2 and Sulphur

Hydrogen Sulphide Decomposition Using Modified Aluminas

Electrolysis of H_2S in Alkaline Solution

Chemically Modified Electrodes for the Electrolytic Production of H_2 and S from H_2S

Plasma Chemical Conversion of H_2S to H_2 and S

Microwave-Initiated Decomposition of H_2S

Hydrogen Optimization

Hydrogen Utilization in Bitumen Upgrading

Study on Upgrader Optimization

Multi-stage Hydrotreating of Athabasca Bitumen

Wide-Cut Cold Lake Blend Distillate Hydrotreating Study

Hydrogen Separation

High-Temperature Separation of Hydrogen Using Novel Ceramic Membranes

High-Efficiency Hydrogen Separation and Production

Appendices

All research projects supported by the Alberta Hydrogen Research Program are listed in Appendix A, while information about the funding provided by the Alberta/Canada Energy Resources Research Fund (A/CERRF) and the Alberta Department of Energy is found in Appendix B.

Appendix A

Complete Listing of Projects Supported by the Alberta Hydrogen Research Program

Project	Researcher	Status
Hydrogen Production		
Examination of the Partial Oxidation of Methane for the Production of Hydrogen and/or Synthesis Gas	G.A. Karim, The University of Calgary, Calgary	Completed in 1989/90
A Claus Plant Modification for Hydrogen Production	Alberta Sulphur Research Ltd., Calgary	Continuing
Conversion of Hydrogen Sulphide to Hydrogen and Organosulphur Compounds by Metal Catalysts	Alberta Sulphur Research Ltd., Calgary	Completed in 1990/91
Production of Hydrogen and Sulphur from Hydrogen Sulphide	L.G. Hepler, University of Alberta, Edmonton and J. Donini, CANMET, Devon	Completed in 1990/91
High-Temperature Electrolysis of Aqueous Hydrogen Sulphide for the Production of Hydrogen and Molten Sulphur	Alberta Research Council, Edmonton	Completed in 1990/91
Chemically Modified Electrodes for Hydrogen Sulphide Electrolysis	Alberta Research Council, Edmonton	Completed in 1991/92
The Carbon Monoxide Catalyzed Conversion of Hydrogen Sulphide to Hydrogen and Sulphur	O.P. Strausz, University of Alberta, Edmonton	Continuing

Cold Plasma Decomposition of Hydrogen Sulphide	Shell Canada Limited, Calgary and Atomic Energy of Canada Limited, Chalk River	Completed in 1992/93
Microwave-Initiated Decomposition of Hydrogen Sulphide	O.P. Strausz, University of Alberta, Edmonton	Completed in 1992/93
Electrolysis of H_2S in Alkaline Solution	Shell Canada Limited, Calgary and CANMET, Devon	Continuing
Hydrogen Sulphide Decomposition Using Modified Aluminas	Alberta Research Council, Devon	Completed in 1992/93

Hydrogen Separation

Hydrogen Separation and Purification	Alberta Research Council, Edmonton	Completed in 1990/91
High-Temperature Separation of Hydrogen Using Novel Ceramic Membranes	Alberta Research Council, Devon	Completed in 1992/93?
High-Efficiency Hydrogen Separation and Production	Highquest Engineering Inc., Vancouver	Continuing

Infrastructure, Storage and Transportation

Hydrogen Producer/ Consumer Network	Alberta Research Council, Devon	Completed in 1990/91
Salt Cavern Storage of Hydrogen	RTM Engineering Ltd., Calgary	Completed in 1990/91
Hydrogen Transportation Using Present Pipeline Networks	Hydrogen Industry Council, Calgary	Completed in 1991/92

Hydrogen Use

Optimization of Hydrogen Utilization in Heavy Hydrocarbon Processing	Alberta Chamber of Resources, Edmonton	Completed in 1991/92
Refinery By-product Hydrogen Use for Electricity Generation in Fuel Cells	TransAlta Utilities Corporation, Calgary	Completed in 1990/91
Hydrogen Utilization in Bitumen Upgrading	Alberta Chamber of Resources, Edmonton	Completed in 1992/93
Multi-stage Hydrocracking of Athabasca Bitumen and Cracked Products	Syncrude Canada Ltd., Edmonton	Continuing
Upgrader Optimization	Alberta Chamber of Resources, Edmonton	Completed in 1992/93
Wide-Cut Cold Lake Blend Distillate Hydrotreating Study	Imperial Oil Resources Limited, Calgary	Completed in 1992/93
Hydrogen Peroxide by Direct Oxidation of Hydrogen	Albchem Industries Ltd., Edmonton	Continuing

Special Projects

Hydrogen Technology Program Planning and Implementation Assistance	Harold V. Page, Edmonton	Completed in 1990/91
The University of Calgary Hydrogen Industry Chair	The University of Calgary, Calgary	Continuing
Hydrogen Research Program Workshop	Info-Tech Conference Management, Calgary	Completed in 1991/92
Hydrogen Research Program Workshop	Info-Tech Conference Management, Calgary	Completed in 1992/93
Resistance of Thermal Spray Coatings to Hydrogen Penetration	Centre for Frontier Engineering Research, Edmonton	Continuing
Japan-Canada Hydro-Hydrogen Pre-feasibility Study	Hydrogen Industry Council, Montreal	Completed in 1992/93

Appendix B - Alberta Hydrogen Research Program: Summary of Expenditures ($)[1]

PROJECT	1987-1989	1989/90	1990/91	1991/92	1992/93	Projected[a] 1993/94	TOTAL
Hydrogen Production							
A Claus Plant Modification for Hydrogen Production	-	68 490	143 847	145 836	164 000	100 000	622 173
Production of Hydrogen and Sulphur from Hydrogen Sulphide	-	76 235	70 665	-	-	-	146 900
Conversion of H_2S to H_2 and Organosulphur Compounds by Metal Catalysts	-	12 806	17 194	-	-	-	30 000
Examination of the Partial Oxidation of Methane for the Production of Hydrogen and/or Synthesis Gas	-	58 391	-	-	-	-	58 391
High-Temperature Electrolysis of Aqueous Hydrogen Sulphide	-	-	60 000	-	-	-	60 000
The CO-Catalyzed Conversion of H_2S to H_2 & Sulphur	-	-	81 640	13 800	24 474	24 500	144 414
Cold Plasma Decomposition of H_2S	-	-	194 627	194 819	37 745	-	427 191
Chemically Modified Electrodes for Hydrogen Sulphide Electrolysis	-	-	25 393	26 488	-	-	51 881
Microwave-Initiated Catalytic Decomposition of Hydrogen Sulphide	-	-	-	60 794	57 878	-	118 672
Electrolysis of H_2S in Alkaline Solution	-	-	-	-	41 795	89 997	131 792
Hydrogen Sulphide Decomposition Using Modified Aluminas	-	-	-	-	37 934	-	37 934
Subtotal Hydrogen Production	0	215 922	593 366	441 737	363 826	214 497	1 829 348
Hydrogen Storage and Transportation							
Salt Cavern Storage of Hydrogen	-	43 071	-	-	-	-	43 071
Hydrogen Producer/ Consumer Network	-	39 492	-	-	-	-	39 492
Hydrogen Transportation, Using Present Pipeline Networks	-	-	56 324	77 525	-	-	133 849
Subtotal Hydrogen Storage and Transportation	0	82 563	56 324	77 525	0	0	216 412

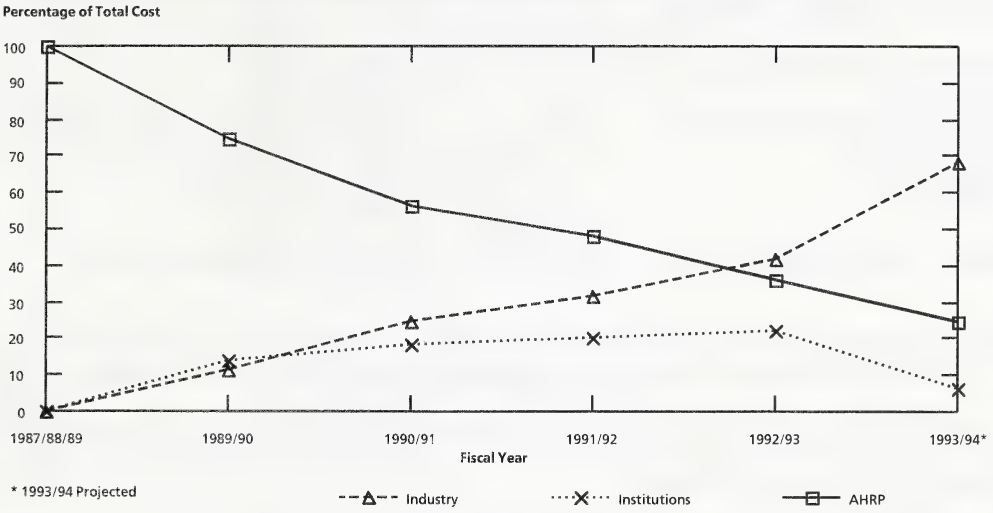
[1] Does not include funding by industry and/or institutions.

PROJECT	1987-1989	1989/90	1990/91	1991/92	1992/93	Projected[a] 1993/94	TOTAL
Hydrogen Separation							
Hydrogen Separation and Purification	-	167 342	116 454	-	-	-	283 796
High-Temperature Separation of H_2 Using Novel Ceramic Membranes	-	-	58 511	65 185	80 027	-	203 723
High-Efficiency Hydrogen Separation and Production	-	-	-	-	92 178	131 040	223 218
Subtotal Hydrogen Separation	0	167 342	174 965	65 185	172 205	131 040	710 737
Hydrogen Use							
Optimization of H_2 Utilization in Heavy Hydrocarbon Processing	-	-	93 246	-	-	-	93 246
Refinery By-product Hydrogen Use for Electricity Generation in Fuel Cells	-	-	15 075	-	-	-	15 075
Hydrogen Utilization in Bitumen Upgrading	-	-	-	43 000	-	-	43 000
Upgrader Optimization	-	-	-	-	35 000	-	35 000
Multi-stage Hydrocracking of Athabasca Bitumen and Cracked Products	-	-	-	-	130 000	-	130 000
Wide-Cut Cold Lake Blend Distillate Hydrotreating Study	-	-	-	-	43 500	-	43 500
Hydrogen Peroxide by Direct Oxidation of Hydrogen	-	-	-	-	40 000	110 525	150 525
Subtotal Hydrogen Use	0	0	108 321	43 000	248 500	110 525	510 346
Special Projects							
Hydrogen Technology Inventory Study for Alberta	47 874	-	-	-	-	-	47 874
Hydrogen Technology Program Planning and Implementation Assistance	5 805	-	-	-	-	-	5 805
The University of Calgary Hydrogen Industry Chair	-	-	375 000[b]	-	-	-	375 000
Hydrogen Workshop 1991	-	-	-	4 950	-	-	4 950
Hydrogen Workshop 1992	-	-	-	-	5 095	-	5 095
Hydrogen Workshop 1993	-	-	-	-	-	1 000	1 000
Japan-Canada Hydro-Hydrogen Pre-feasibility Study	-	-	-	-	24 860	-	24 860
Resistance of Thermal Spray Coatings to Hydrogen Penetration	-	-	-	-	29 070	-	29 070
Subtotal Special Projects	53 679	0	375 000[b]	4 950	59 025	1 000	493 654
TOTAL Alberta Hydrogen Research Program	53 679	465 827	1 307 976[b]	632 397	843 556	457 062	3 760 497

[a] Projected expenditures for projects active in 1992/93 and continuing in 1993/94; do not include projects commencing in 1993/94. Total expenditures for new and continuing projects in 1993/94 are projected to be $1.1 million.

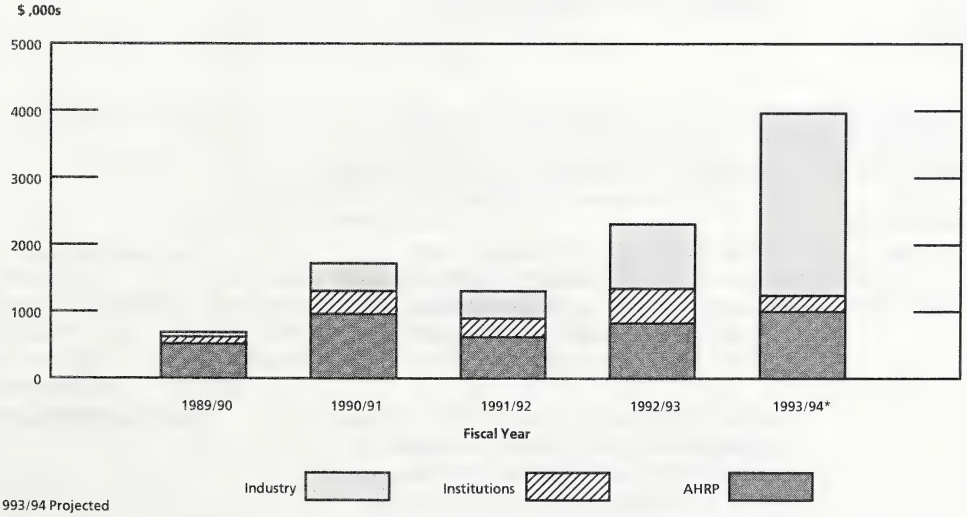
[b] Advanced transfer of $375 000 to The University of Calgary Hydrogen Industry Chair

Alberta Hydrogen Research Program
Funding Trend



* 1993/94 Projected

Alberta Hydrogen Research Program
Total Cost of Projects



* 1993/94 Projected

Appendix C - Project Reports

Many of the following project reports are classified as non-confidential and are available for review at two loactions in Edmonton:

Research and Technology Branch Library
Alberta Energy
11th Floor, North Petroleum Plaza
9945 - 108 Street
Edmonton, Alberta
T5K 2G6

Telephone: (403) 427-8042

Library Services
Alberta Energy
9th Floor, South Petroleum Plaza
9915 - 108 Street
Edmonton, Alberta
T5K 2C9

Telephone : (403) 427-7425

Confidential reports may be available, but their availability is subject to approval by the research performer and Alberta Energy. Contact Alberta Energy for more information.

Reports marked with an asterisk are in conference proceedings, or are articles published in scientific journals, and are available from appropriate technical and university libraries. They are not available from Alberta Energy.

Project	Project Report(s)	Availability
Hydrogen Technology Inventory Study for Alberta	RTM Engineering Ltd. 1988. *Alberta Hydrogen Technology Inventory.*	Non-confidential
Examination of the Partial Oxidation of Methane for the Production of Hydrogen and/or Synthesis Gas	Karim, G.A. 1990. *Examination of the Partial Oxidation of Methane for the Production of Hydrogen and for Synthesis Gas.* The University of Calgary.	Non-confidential
	Karim, G.A. and A.S. Hanafi. 1991. *An Analytical Examination of the Partial Oxidation of Rich Mixtures of Methane and Oxygen.* Fossil Fuel Combustion. 33:127-133.	Non-confidential*
	Karim, G.A. and G. Zhou. 1993. *A Kinetic Investigation of the Partial Oxidation of Methane for the Production of Hydrogen.* Int. J. Hydrogen Energy. 18:125-129.	Non-Confidential*

Project	Project Report(s)	Availability
	Karim, G.A. and G. Zhou. 1992a. *The Uncatalyzed Partial Oxidation of Methane for the Production of Hydrogen with Recirculation.* Fossil Fuel Combustion. 39:77-84.	Non-confidential*
	Karim, G.A. and G. Zhou. 1992b. *A Kinetic Investigation of the Partial Oxidation of Methane for the Production of Hydrogen.* Presented at 9th World Hydrogen Energy Conference, Paris, France. June 22-25, 1992.	Non-confidential*
A Claus Plant Modification for Hydrogen Production	Dowling, N.I. and J.B. Hyne. 1993. *A Claus Furnace Modification to Produce Both Sulfur and Hydrogen from* H_2S. Sulphur '93, Hamburg, Germany. April 4-7.	Non-confidential*
	Dowling, N.I., J.B. Hyne, D.L. Moon and C.S.C. Lau. 1993a. *A Claus Plant Modification for Hydrogen Production.* Report for October-December 1992. Alberta Sulphur Research Ltd.	Confidential - project continuing
	Dowling, N.I., J.B. Hyne, D.L. Moon and C.S.C. Lau. 1993b. *A Claus Plant Modification for Hydrogen Production.* Report for January-March 1993. Alberta Sulphur Research Ltd.	Confidential - project continuing
	Dowling, N.I., J.B. Hyne, D.L. Moon and C.S.C. Lau. 1992. *A Claus Plant Modification for Hydrogen Production.* Final A/CERRF Report. Alberta Sulphur Research Ltd.	Confidential - project continuing
Conversion of Hydrogen Sulphide to Hydrogen and Organosulphur Compounds by Metal Catalysts	Clark, P.D. 1991. *Investigations Into the Conversion of* H_2S *to* H_2 *and Organosulphur Compounds by Metal Catalysis.* Alberta Sulphur Research Ltd.	Confidential until July 1996

Project	Project Report(s)	Availability
	Clark, P.D. and B. Wassink. 1990. *A Review of Methods for the Conversion of H_2S to Sulphur and Hydrogen.* In: Alberta Sulphur Research Ltd. Quarterly Bulletin XXVI:1 77. Alberta Sulphur Research Ltd.	Non-confidential
Production of Hydrogen and Sulphur from Hydrogen Sulphide	Chen, Q., L. Li and L.G. Hepler. 1990. *Kinetics of Desulfurization of Hydrogen Sulphide Using Metallic Copper as a Desulfurizer.* Accepted for publication by Can. J. Chem. Eng.	Non-confidential
High-Temperature Electrolysis of Aqueous Hydrogen Sulphide for the Production of Hydrogen and Molten Sulphur	Gray, L.G.S. and M.J. Danysh. 1991. *High Temperature Electrolysis of Aqueous Hydrogen Sulphide for the Production of Hydrogen and Molten Sulfur.* Alberta Research Council.	Non-confidential
Chemically Modified Electrodes for the Electrolytic Production of Hydrogen and Sulphur from Hydrogen Sulphide	Petrovic, S. 1991. *Chemically Modified Electrodes for the Electrolytic Production of Hydrogen and Sulphur from Hydrogen Sulphide.* Alberta Research Council.	Confidential until Mar. 31, 1994
The Carbon Monoxide Catalyzed Conversion of H_2S to H_2 and S.	Strausz, O.P. 1993. *The CO-Catalyzed Conversion of H_2S to H_2 and S.* Final Report. April 1, 1992-March 31, 1993. University of Alberta.	Confidential - project continuing
	Strausz, O.P. 1991. *The CO-Catalyzed Conversion of H_2S to H_2 and S.* April 1, 1990-March 31, 1991. University of Alberta.	Confidential - project continuing
	Torres, M.E., E. Yildirim, F. Faraji and O.P. Strausz. 1993. *Novel Processes for the Conversion of H_2S to H_2 and S.* Proceedings of Oil Sands: Our Petroleum Future Conference, April 4-7, 1993. Edmonton, Alberta.	Non-confidential*

Project	Project Report(s)	Availability
Cold Plasma Decomposition of Hydrogen Sulphide	Craw, M.T., K.D. McCrimmon, R.P. Tremblay, R.M. Hutcheon and E. Luinstra. 1992. *Microwave Decomposition of Hydrogen Sulphide.* 10th Anniversary Conference, Hydrogen Industry Council. Kananaskis, Alberta, May 20-21, 1992.	Non-confidential
	Craw, M.T., L.J. Cornett, K.D. McCrimmon and R.M. Hutcheon. 1991. *Cold Plasma Decomposition of Hydrogen Sulphide.* Final Report to A/CERRF. AECL Research/Shell Canada Limited.	Confidential until Mar. 31, 1995
	Craw-Ivanco, M.T., L.J. Cornett, K.D. McCrimmon, R.P. Tremblay and R.M. Hutcheon. 1993. *Cold Plasma Decomposition of Hydrogen Sulphide.* AECL Report RC-969.	Confidential until Mar. 31, 1995
	Craw-Ivanco, M.T. and E. Luinstra. 1992. *Cold Plasma Decomposition of Hydrogen Sulphide.* H_2 Workshop '92. Calgary, Alberta, October 8, 1992.	Non-confidential*
	Craw-Ivanco, M.T. and J.H. Rowat. 1993. *Review of Available Russian Literature Relating to Hydrogen Sulphide Decomposition in a Microwave/Radiofrequency Plasma.* AECL Report RC-905.	Confidential until Mar. 31, 1995
	Luinstra, E.A., R.S. Czura and P.M. Davies, 1993. *Cold Plasma Decomposition of Hydrogen Sulphide.* Shell Canada Limited.	Confidential until Mar. 31, 1995
Microwave-Initiated Decomposition of Hydrogen Sulphide	Strausz, O.P. 1993. *Microwave-Initiated Decomposition of Hydrogen Sulphide.* Final Report. April 1, 1992-March 31, 1993. University of Alberta.	Confidential until Mar. 31, 1995

Project	Project Report(s)	Availability
Electrolysis of H_2S in Alkaline Solution	Petrovic, S., P. Komorowski, K. Michaelian, C.K. Preston, J. Szynkarczuk, S. Thind, R. Willier, J. Donini and E.A. Luinstra. 1993. *Electrolysis of H_2S in Alkaline Solutions.* Division Report WRC 93-01 (CF). CANMET.	Confidential - project continuing
	Petrovic, S., P. Komorowski, K. Michaelian, J. Szynkarczuk, S. Thind, R. Willier and J. Donini. 1992. *Electrolysis of H_2S in Alkaline Solutions.* Division Report WRC 92-00 (CF). CANMET.	Confidential - project continuing
	Petrovic, S., P. Komorowski. K. Michaelian, J. Szynkarczuk, S. Thind, R. Willier, J. Donini and E. Luinstra. 1992. *Electrolysis of H_2S in Alkaline Solutions.* Third Quarter Report. October 1-December 3, 1992. Shell Canada Limited.	Confidential - project continuing
Hydrogen Sulphide Decomposition Using Modified Aluminas	McFarlane, R.A. 1992d. *Hydrogen Sulphide Decomposition Using Modified Aluminas.* Final Report. Alberta Research Council	Confidential until March 31, 1995
Hydrogen Separation and Purification	Pan, C.Y., E. Hadfield and C.McMinis. 1991 *Final Technical Report on Hydrogen Separation and Purification.* Alberta Research Council	Confidential until July 1996
High-Temperature Separation of Hydrogen Using Novel Ceramic Membranes	Rangwala, H.A. and E. Taylor. 1993. *High Temperature Separation of Hydrogen Using Novel Ceramic Membranes.* Final Report (1992-1993). Alberta Research Council.	Confidential until March 1995
	Rangwala, H.A. and L. Johanson. 1992. *High Temperature Separation of Hydrogen Using Novel Ceramic Membranes.* Alberta Research Council.	Confidential until March 1995
	Smith, K.J. and L. Johanson. 1991a. *Development of Ceramic Membranes for High Temperature Separation of Hydrogen. A Review.* Alberta Research Council.	Confidential until March 1995

Project	Project Report(s)	Availability
	Smith, K.J. and L. Johanson. 1991b. *High Temperature Separation of Hydrogen Using Novel Ceramic Membranes.* Alberta Research Council.	Confidential until March 1995
High-Efficiency Hydrogen Separation and Production	Keefer, B.G. 1993. *TCPSA Pilot Plant Demonstration Program.* Phase A Report. Highquest Engineering Inc.	Confidential - project continuing
Hydrogen Producer/ Consumer Network	Kovacik, G., B. Özüm and M. Oğuztöreli. 1990. *Hydrogen Producer/Consumer Networking Transportation and Storage Optimization.* Alberta Research Council.	Confidential until May 1, 1994
Salt Cavern Storage of Hydrogen	RTM Engineering Ltd. 1990. *Salt Cavern Storage of Hydrogen.*	Confidential until April 1997
Hydrogen Transportation Using Present Pipeline Networks	Colt Engineering Corporation. 1991. *Hydrogen Transportation Using Present Pipeline Network Study. Volume III. Collection, Distribution and Use in Alberta.* Prepared for Hydrogen Industry Council.	Confidential until Dec. 31, 1993
	DB Robinson Research Ltd. 1991. *Hydrogen Transportation Using Present Pipeline Network Study. Volume I. Thermodynamic and Combustion Data.* Prepared for Hydrogen Industry Council.	Non-confidential
	Hydrogen Industry Council. 1991. *Summary of Hydrogen Transportation Using Present Pipeline Network Study.*	Confidential until Dec. 31, 1993
	Law, Sigurdson & Associates. 1991a. *Hydrogen Transportation Using Present Pipeline Network Study. Volume IV. Collection, Distribution and Use Beyond Alberta.* Prepared for Hydrogen Industry Council.	Confidential until Dec. 31, 1993

Project	Project Report(s)	Availability
	Law, Sigurdson & Associates. 1991b. *Hydrogen Transportation Using Present Pipeline Network Study. Volume V. Collection, Distribution and Use Beyond Alberta. Appendices.* Prepared for Hydrogen Industry Council.	Confidential until Dec. 31, 1993
	SKM Consulting Ltd. 1991. *Hydrogen Transportation Using Present Pipeline Network Study. Volume II. Pipeline and Compressors Purification, Storage and Generation. Hydrogen-Natural Gas Mixture for Fuel Cells.* Prepared for Hydrogen Industry Council.	Non-confidential
Optimization of Hydrogen Utilization in Heavy Hydrocarbon Processing	McCann, T.J. 1991. *Optimum Hydrogen Use in Upgrading and Refining.* Prepared for Oil Sand Task Force, Alberta Chamber of Resources. RTM Engineering Ltd.	Non-confidential
Refinery By-product Hydrogen Use for Electricity Generation in Fuel Cells	Patterson, R.J. and T.J. McCann. 1991. *Refinery Byproduct Hydrogen Use for Electricity Generation in Fuel Cells.* RTM Engineering Ltd. for TransAlta Utilities Corporation.	Non-confidential
Hydrogen Utilization In Bitumen Upgrading	Dettman, H.D. and D.J. Patmore and S.H. Ng 1993. *Hydrogen Utilization in Bitumen Upgrading: An Experimental Study of the Fate of Process Hydrogen. Final Report.* CANMET.	Confidential until Dec. 31,
	Dettman, H.D., D.J. Patmore and S.H. Ng. 1993b. *The Fate of Process Hydrogen in Bitumen Upgrading.* In: Proceedings of Oil Sands: Our Petroleum Future. Edmonton, April 4-7, 1993.	Non-confidential
Multi-stage Hydrocracking of Athabasca Bitumen and Cracked Products	Sanford, E.C. 1993a. *Mechanism of Coke Prevention by Hydrogen During Residuum Hydrocracking.* 205th National Meeting, American Chemical Society, Denver, CO, March 28-April 2, 1993.	Non-confidential*

Project	Project Report(s)	Availability
	Sanford, E.C. 1993b. *Multistage Hydrocracking of Athabasca Bitumen and Cracked Products.* Fourth Quarter Progress Report. January-March 1993. Syncrude Canada Ltd.	Confidential - project continuing
	Sanford, E.C. 1992a. *Catalyst Selectivity During Hydrocracking: The Effect of Temperature, Pressure and Time on Bitumen Conversion and Catalyst Deactivation in a Batch Stirred Tank Reactor.* First Quarter Report. April-June 1992. Syncrude Canada Ltd.	Confidential - project continuing
	Sanford, E.C. 1992b. *A Molecular Approach to Understanding Residuum Conversion During Coking, Hydrocracking and Hydrogenolysis Hydrocracking of Athabasca Bitumen Over a Wide Range of Conversions.* Syncrude Canada Ltd.	Confidential - project continuing
	Sanford, E.C. 1992c. *Influence of Hydrogen and Catalyst on the Removal of Heteroatoms, Aromatics and CCR During Cracking of Athabasca Bitumen Residuum Over a Wide Range of Conversions.* Syncrude Canada Ltd.	Confidential - project continuing
Upgrader Optimization	Alberta Chamber of Resources Oil Sands Task Force. *Upgrader Optimization. A New Look at the Regional Upgrader with Selected Additions.*	Non-confidential
	McCann, T.J. 1991. Optimum Hydrogen Use in Upgrading and Refining. Prepared for Oil Sand Task Force, Alberta Chamber of Resources. RTM Engineering Ltd.	Non-confidential
Wide-Cut Cold Lake Blend Distillate Hydrotreating Study	Ghosh, M., S.E. McGregor, C.A. Swift, A. Ravella and D.W. Kraemer. 1992. *Wide-Cut Cold Lake Blend Hydrotreating Study.* Imperial Oil Resources Ltd.	Confidential until March 31, 1995
Japan-Canada Hydro-Hydrogen Pre-feasibility Study	Hydrogen Industry Council. 1993. *Japan-Canada Joint Techno-Economic Analysis for A Clean Energy Supply System Between Japan and Canada.* Prepared for Hydrogen Industry Council and funding parties.	Non-Confidential

Appendix D - Industry Partners

Albchem Industries Ltd	Operating at Bruderheim, Alberta since 1991, Albchem Industries Ltd. produces sodium chlorate, an environmentally preferred alternative to chlorine for pulp bleaching. Hydrogen is a by-product of Albchem's production process.
Alberta Chamber of Resources (ACR)	For 57 years, ACR has represented the interests of private-sector resource companies operating in Alberta. Currently, ACR represents 130 corporate members who are concerned with oil sands, coal, oil and gas, forestry, chemicals, and industrial and metallic minerals. Many of these resource activities depend on a stable, cost-effective supply of hydrogen.
Alberta Sulphur Research Ltd. (ASRL)	Founded in 1964 and located at The University of Calgary, ASRL is a non-profit research organization supported by nearly 30 companies engaged directly or indirectly in the production, handling and transportation of elemental sulphur. More than 90 per cent of Alberta's sulphur-producing industries are active members of ASRL. All use the Claus Process to recover sulphur from H_2S.
Canadian Occidental Petroleum Ltd	A diversified company with worldwide interests and operations in oil, gas, alternate fuels and chemicals, CanadianOxy has substantial oil, gas and chemical operations in Alberta that produce or use hydrogen.
Centre for Frontier Engineering Research (C-FER)	Established in 1983 as a not-for-profit joint venture in industrial research, C-FER is funded by approximately 30 companies, government agencies and universities. C-FER specializes in theoretical and experimental research concerning engineering materials and systems.
Highquest Engineering Inc	Founded in 1984 and based in Vancouver, Highquest specializes in the development of energy-conversion and fluid-separation technology. Research has focused on hydrogen separation and gas separation in fuel cell systems.

Hydrogen Industry Council (HIC)	Based in Montreal, with a western office in Calgary, the Hydrogen Industry Council represents Canadian companies and agencies concerned with hydrogen. Approximately 15 per cent of HIC's members are in Alberta.
Imperial Oil Resources Limited	As the resource extraction arm of Imperial Oil Limited, Imperial Oil Resources Limited operates crude oil, natural gas and bitumen-production facilities, and is one of the participants in the Syncrude Canada operation. Hydrogen is a key feedstock in Imperial Oil's overall interests.
Shell Canada Limited	A leading Canadian oil, natural gas and petrochemical company, Shell Canada Limited is developing the Caroline natural gas field which contains gas having an H_2S content of approximately 35 per cent.
Sherritt Gordon Ltd.	An integrated company based in Alberta, Sherritt produces fertilizers and chemicals, extracts oil and gas, refines nickel and cobalt, and develops advanced industrial materials and metallurgical technologies. Hydrogen is used in several areas of Sherritt's operations.
Syncrude Canada Ltd	As the world's largest producer of synthetic crude oil, Syncrude Canada Ltd. requires significant quantities of hydrogen to upgrade bitumen to "syncrude." New upgrading processes being investigated will require even greater amounts of hydrogen.

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